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**APPLICATION NUMBER: 60/545,415**

**FILING DATE: February 18, 2004**

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This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)					
Given Name (first and middle [if any])		Family Name or Surname		Residence (City and either State or Foreign Country)	
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Additional inventors are being named on the _____ separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
NON-COVALENT BONDING AGENT FOR CARBON NANOTUBE REINFORCED POLYMER COMPOSITES					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
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Respectfully submitted,

[Page 1 of 2]

Date 2/18/04

SIGNATURE \_\_\_\_\_

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NON-COVALENT BONDING AGENT  
FOR CARBON NANOTUBE REINFORCED POLYMER COMPOSITES

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AKERMAN SENTERFITT DOCKET NO. 5853-485

## CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] Not applicable.

## STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

## FIELD OF THE INVENTION

[0003] The invention relates to carbon nanotube reinforced polymer composite materials and methods for making the same.

## BACKGROUND OF THE INVENTION

[0004] There is a never ending search for improved materials. Many of these improved materials are composite materials. Polymer composites comprising a polymer matrix having one or more additives, such as a particulate or fiber material, dispersed throughout the continuous polymer matrix are well known. The additive is often added to enhance one or more properties of the polymer, such as the tensile strength.

[0005] A carbon nanotube is essentially a graphite sheet folded into a tubular shape. This structure retains the mechanical strength of the sheet axial to the orientation of the tube, but is very weak in the lateral direction. Studies have estimated the potential engineering axial modulus of these nanotubes between about 300 Gigapascals to 1 Terapascal. One of the strongest engineering polymer fibers known, SPECTRA®, possesses a modulus of roughly 300

Efforts to harness this strength in any practical engineering application has thus far been largely unsuccessful, due to the great difficulties in producing nanotubes in pure form, and also in arranging them in a manner that can be utilized. Recent efforts have shifted to combining nanotubes into a polymer matrix, much like a fiberglass composite, using carbon nanotubes in place of glass. Certain processing can create polymer threads with an aligned nanotube strengthening phases, but mechanical testing has shown limited improvements in strength compared to theoretical predictions. It is thought that insufficient bonding between the nanotube and polymer phases limits the transfer of stress between the respective phases, and thus the ability of the nanotube phase to reinforce the polymer phase of the composite.

[0006] Chemical substitution of active groups onto the nanotube structure has also been investigated as a possible way of improving bonding at the nanotube polymer interface. However, chemical substitution can significantly reduce the strength and adversely affect the unique characteristics of the nanotube structure, such as the electrical conductivity of the nanotube.

## SUMMARY

**[0007]** A carbon nanotube polymer composite material includes a polymeric solid state continuous phase comprising a plurality of polymer chains, a plurality of carbon nanotubes dispersed in the continuous phase, and a bonding agent for mechanically coupling the polymer chains to the nanotubes. The bonding agent joins the polymer chain to the nanotube and is non-covalently bond to the nanotube surface. The nanotubes can be single wall nanotubes (SWNTS) or multi wall nanotubes (MWNTS).

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0008]** A fuller understanding of the present invention and the features and benefits thereof will be obtained upon review of the following detailed description together with the accompanying drawings, in which:

**[0009]** Figure 1 shows the structure of an exemplary bonding agent comprising a polymer bonding group bound to a nanotube non-covalent bonding group comprising a pyrenyl group, according to an embodiment of the invention.

**[00010]** Figure 2 shows alternate exemplary non-covalent bonding group.

**[00011]** Figure 3(a) shows a schematic of a composite according to the invention where the bonding agent is incorporated into the polymer chain and forms a bridge to the nanotube, while FIG. 3(b) shows the bonding agent forming a bridge between a nanotube and a polymer chain without being incorporated in the polymer chain.

**[00012]** Figure 4 shows a schematic of a carbon nanotube reinforced polymer composite including carbon nanotubes aligned in a continuous polymer phase, where the polymer is joined to the nanotube by bonding agent molecules.



## DETAILED DESCRIPTION

**[00013]** A carbon nanotube polymer composite material includes a polymeric solid state continuous phase comprising a plurality of polymer chains, a plurality of carbon nanotubes dispersed in the continuous phase, and a bonding agent for mechanically coupling the polymer chains to the nanotubes. The bonding agent is joined to both the polymer chain and to the nanotube. The nanotubes can be single wall nanotubes (SWNTS), multi wall nanotubes (MWNTS), or a combination of SWNTS and MWNTS.

**[00014]** Polymers can be selected from a broad range of polymers for use with the invention, depending on the intended application. Polymers can also include biocompatible polymers, such as for certain health care related application. For example, polymers can include rubber, polyester, polystyrene, latex, polyethylene, epoxies, and polyacrylates.

**[00015]** For health care applications the polymer used must be biocompatible and fulfill certain requirements. All such polymers must be chemically inert, noncarcinogenic, hypoallergenic, and generally mechanically stable. Regarding use of the polymer in a polymer composite as an implant material, the material should not be physically or chemically modified by local tissue, and the implant should not cause any inflammatory response at the site of implantation. Biocompatible synthetic and non-degradable polymers include silicone elastomers, poly(ethylene-co-vinyl acetate), and polyacrylates, such as poly isobutylcyanoacrylate and poly isohexylcyanoacrylate, and poly(methyl methacrylate).

**[00016]** The awkward arrangement of the sheets in graphite comprising the nanotubes make it very difficult for the nanotubes to realize their full application potential in engineering applications. However, based on the invention, the high aspect ratio, small diameter, low weight, high mechanical strength, high thermal and stability in air, and high electrical and thermal

conductivity provided by nanotubes can be exploited as the high performance carbon fibers for high performance, multifunctional composites.

**[00017]** In contrast to previous efforts which have covalently bonded functional groups to the nanotube to provide a desired characteristic to the resulting structure not available from the nanotube itself, the invention provides a way to improve bonding between the nanotube surface and any number of polymer substrates without covalently bonding to the nanotube. Covalent bonding is known to damage or otherwise change the  $\pi$ - $\pi$  conjugated nanotube structure. Using the disclosed bonding agent which comprises a short polymer chain with active groups on each end, one end will non-covalently bond with the nanotube strengthening phase, and the other end will bond to the polymeric continuous phase substrate material.

**[00018]** One method of bonding molecules to nanotubes using a bonding agent is disclosed in Chen et al. J. Am. Chem. Soc., 2001, 123, 3838 (hereafter Chen). Chen discloses a method for bonding protein markers to nanotube surfaces using a bonding agent. Figure 1 shows the structure of the bonding agent disclosed by Chen. The invention is in no way limited to this particular bonding agent.

**[00019]** The bonding agent shown in FIG. 1 comprises a multifunctional molecule that includes a planar pyreny group which is a small piece of graphite sheet on one end and a polymer compatible active end group on the other end, the respective functional end groups bound together with a short alkane chain. The planar pyreny group is capable of non-covalently bonding to the surface of the nanotube through a phenomenon known as  $\pi$ -stacking, where bonds within the pyreny structure interact strongly with  $\pi$  bonds within the nanotube without altering the chemical structure or bonding arrangement of the nanotube.

**[00020]** Pi stacking more generally involves overlap of  $\pi$  bonds between respective aromatic side chains which results in electron delocalization including both side chains. This interaction produces an energy minimum thereby stabilizing the structure. A  $\pi$ -stacking attachment of a given bonding agent molecule to carbon nanotubes does not degrade the nanotubes, in contrast to methods which involve covalent bonding. In addition, pi-stacking works with virtually any diameter nanotube and is inherent in the backbone of rigid conjugated polymers.

**[00021]** As note above, the bonding agent can be a variety of molecular structures which include one end group which can bond to the polymer or be included in the polymer chain and another end group which is capable of non-covalently bonding to the surface of the nanotube. Bonding agents can be designed to bind the nanotube and a given polymer of interest. For example, to impregnate a polymer fiber with a nanotube strengthening phase, a bonding agent having a polymer bonding group bound to a nanotube non-covalent bonding group can be synthesized.

**[00022]** Aromatic end group moieties are generally preferred as the non-covalent bonding group as they can provide a pi-stacking interaction with the nanotube. Figure 2 shows a hypothetical sulfur comprising aromatic, respectively, which can pi-stack with nanotubes.

**[00023]** The polymer compatible active group of the bonding agent can be designed to interact with the bulk polymer continuous phase of the composite. Thus, the bonding agent can significantly improve the bonding characteristics between the polymer and nanotube, and thus improve the load transfer between the two phases (polymer and nanotube) within the composite. Both active ends of the bonding agent can be modified to suit the intended application.

**[00024]** The polymer composite according to the invention can be formed using a variety of processing variants. In one embodiment, bonding agent is added to the bulk polymer

precursor, generally in the form of a monomer or oligomer solution. The bulk nanotube material is generally pre-treated with the bonding agent and solvent to aid in nanotube separation and dispersion. The polymer precursor solution is then preferably blended with the nanotube solution. The overall concentration of bonding agent should be so that an excess of bonding agent is provided. In an exemplary embodiment, the final composite material comprises 0.5 % to 10% nanotube by weight.

**[00025]** Polymers, such as epoxies, do not generally require heating to complete polymerization. However, in some embodiments, the mixture is heated to a suitable temperature to complete polymerization. Heating also helps drive off solvent.

**[00026]** In a preferred embodiment, the mixture is then subjected to high amounts of shear to form thin fiber, such as using a gel spinning technique or extrusion. As the fiber is drawn, the nanotubes will orient themselves along the direction of shear, which will result in a strong load bearing orientation within the fiber. If performed correctly, the bonding agent will polymerize into the bulk polymer and associate itself along the surface of the nanotubes, resulting in improved load transfer across the interface, as seen in similar systems employing glass fiber or other contemporary composite systems. It may also be possible to align nanotubes in the composite material using a magnetic field without using a mechanical shear.

**[00027]** Depending on the particular bonding agent and the processing conditions, the bonding agent can be incorporated in the polymer structure, bridge between a polymer chain and a nanotube, or be both incorporated in the polymer structure, and provide bridges between the polymer and the nanotube. Figure 3(a) shows a schematic of a composite according to the invention where the bonding agent ("B") is incorporated into the polymer chain comprised of a repeat unit denoted as "A", while FIG. 3(b) shows the bonding agent (B) forming a bridge

between the nanotube and a polymer chain (A-A-A) without the bonding agent being incorporated in the polymer chain.

**[00028]** Figure 4 shows a schematic of a carbon nanotube reinforced polymer composite rope section 400 including a plurality of carbon nanotubes 410 aligned in a continuous polymer phase comprising a plurality of polymer chains 420, where the polymer chains 420 is joined to the nanotube by bonding agent molecules 425. Some polymer chains 420 are shown mechanically coupling a given nanotube 410 to one or more other tubes 410. It is estimated that the strength of the reinforced composite material can be at least 250 GPa, such as 500 GPa, or more, depending on the particular polymer, bonding agent and nanotubes and percentages of each used, and the specific processing conditions utilized.

**[00029]** Although high-modulus polymer materials, including carbon-fiber reinforced composites are available, the polymer composites according to the invention are structurally distinct and provide several significant advantages over these materials. For example, the invention allows any number of different polymer materials to be used as the continuous phase, providing flexibility that can be tailored to specific end applications. Also, the nanotube strengthening phase can greatly increase the modulus and strength of the polymer base without contributing much, if anything, to density. Also, since the nanotube strengthening component is of a nano-size scale, there is no real limit to the size scale of the end product, and composite thread could conceptually be drawn as thin as practically possible without any loss of strengthening.

**[00030]** Composites including various engineering plastic, epoxy, and adhesive composite can benefit from the invention. The invention can could be used in a wide variety of applications, including high performance nano-composite fiber, which can be bound into cable or woven into

fabric. Thus, potential end products include anything from fishing line to protective clothing, such as a bullet proof vest. Other applications for the invention include, but are not limited to:

- i) electrical applications including electronic circuits;
- ii) thermal management (e.g. interface materials, spacecraft radiators, avionic enclosures and printed circuit board thermal planes);
- iii) aircraft, ship, infrastructure and automotive structures;
- iv) improved dimensionally stable structures for spacecraft and sensors;
- v) reusable launch vehicle cryogenic fuel tanks and unlined pressure vessels;
- vi) packaging of electronic, optoelectronic and microelectromechanical (MEMS) components and subsystems;
- vii) fuel cells; and
- viii) medical materials;

## EXAMPLES

**[00031]** It should be understood that the example and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application. The invention can take other specific forms without departing from the spirit or essential attributes thereof.

**[00032]** As noted above, nanotube strengthening according to the invention can be used for a broad range of applications. The addition of a nanotube strengthening phase could substantially increase modulus of fiber without changing any of the beneficial aspects of the fiber, such as chemical resistance and compatibility with existing additives and coatings. Additionally,

nanotubes can provide added strength without any increase in fiber density. Also, unlike other composite systems, nanotubes exist in the sub-micro scale, thus, fibers can be spun to very thin dimensions, yet retain the strengthening provided by the nanotubes.

[00033] Polymer fibers are commonly used for a wide variety of engineering applications, from braided cable for sports, to woven cloth for clothing, to formed reinforced objects such as helmets. In many of these applications, the key to improved performance is an increase in strength of the polymer fiber, or the ability to absorb energy before straining or breaking.

[00034] Bonding agents can be designed to bind the nanotube and a given polymer of interest. For example, to impregnate a polymer fiber with a nanotube strengthening phase, a bonding agent with the following structure can be synthesized:

[00035] (polymer bonding group)----- (nanotube noncovalent bonding group)

[00036] The Table below provides examples of some thermoplastic polymer matrixes that have been incorporated into other bonding agents already in existence that can be adapted as shown above for use with the invention.

### Thermoplastics

Class type of material to be coupled	Agent class
Cellulosics	amine isocyanate phosphate
Polyacetal	quaternary thiuronium
Polyacrylate	methacrylate ureido
Polyamine (nylon)	amine ureido
Polyamine-imide	amine chloromethylaromatic
Polybutylene terephthalate	amine isocyanate
Polycarbonate	amine
Polyetherketone (ethylene-vinyl acetate) copolymer	amine ureido
Polyethylene	amine styryl vinyl
Polyphenylene oxide	amine aromatic
Polyphenylene sulfide	amine chloromethylaromatic mercapto
Polypropylene	aromatic styryl
Polystyrene	aromatic epoxy vinyl
Polysulfone	amine
Polyvinyl butyral	amine
Polyvinyl chloride	amine alkanolamine

[00037] As another example, if a manufacturer of polycarbonate fiber wishes to manufacture a stronger fiber using nanotubes, a bonding agent having an amine polymer bonding group on one



end and a noncovalent nanotube bonding head on the other end can be used. The amine group will polymerize with the carbonate as the fiber is drawn under appropriate conditions. Thus, the bonding agent will serve as a physical link between the nanotubes and polycarbonate chains, and significantly strengthen the bonding between them, forming a stronger composite.

**[00038]** As yet another example, a manufacturer of nylon fiber can add a nanotube strengthening according to the invention in its product. The invention can be used to provide a stronger nylon based fiber for advanced applications, while still maintaining nylon as the base material. One application for a reinforced nylon is for improved rope and fishing line.

**[00039]** Regarding nylon applications, a non-covalent bonding agent can be specifically designed for nylons, such as one based on an amine active group bound to a pyrenyl group through a short alkane chain. Bulk nanotube and the bonding agent can be incorporated into the fiber spinning process, and various parameters such as bulk nanotube and bonding agent weight contents can be adjusted to achieve the desired performance and cost of the final fiber. Given the proper incorporation of the optimum quantities of bulk nanotube and bonding agent, a fiber can be produced which substantially maintains the same weight, proportions, and chemical behavior of the original fiber, yet possesses substantially greater tensile modulus and toughness. The invention appears to be capable of adding modulus to even some of the strongest engineering polymers known, such as ultra-high molecular weight polyethylene (UHMWPE), and make them even stronger without sacrificing low weight.

**[00040]** While various embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore

intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

## CLAIMS

1. A carbon nanotube polymer composite material, comprising:  
a polymeric solid state continuous phase comprising a plurality of polymer chains;  
a plurality of carbon nanotubes dispersed in said continuous phase, and  
a bonding agent for mechanically coupling said polymer chains to said nanotubes, said bonding agent joined to said both polymer chain and to said nanotube.
2. The composite of claim 1, wherein said bonding agent is non-covalently joined to nanotube.
3. The composite of claim 1, wherein nanotubes are aligned substantially parallel to one another.
4. The composite of claim 1, wherein said composite material is bio-compatible.
5. The composite of claim 1, wherein said nanotubes comprise 1 to 10 wt % of said composite.
6. The composite of claim 3, wherein a modulus of said composite along a direction of said alignment is at least 250 GPa at 25 C.
7. A method for forming carbon nanotube polymer composite materials, comprising the steps of:  
mixing a bonding agent having active groups on each of its ends with a polymer solution to form a functionalized polymer solution comprising one of said ends of said bonding agent bonded to said polymer,

blending said functionalized polymer solution with carbon nanotube material to form a nanotube polymer composite, wherein the other of said ends becomes non-covalently joined to said nanotube.

8. The method of claim 7, further comprising the step of drawing said composite, wherein said nanotubes become arranged substantially parallel to one another.

9. The method of claim 7, wherein said blending step comprises polymerizing said bonding agent into said polymer.

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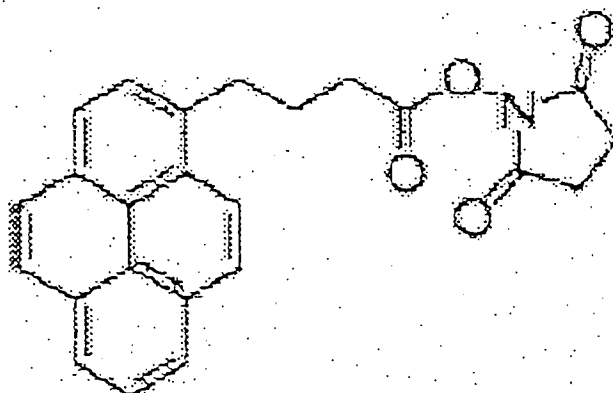


FIG. 1

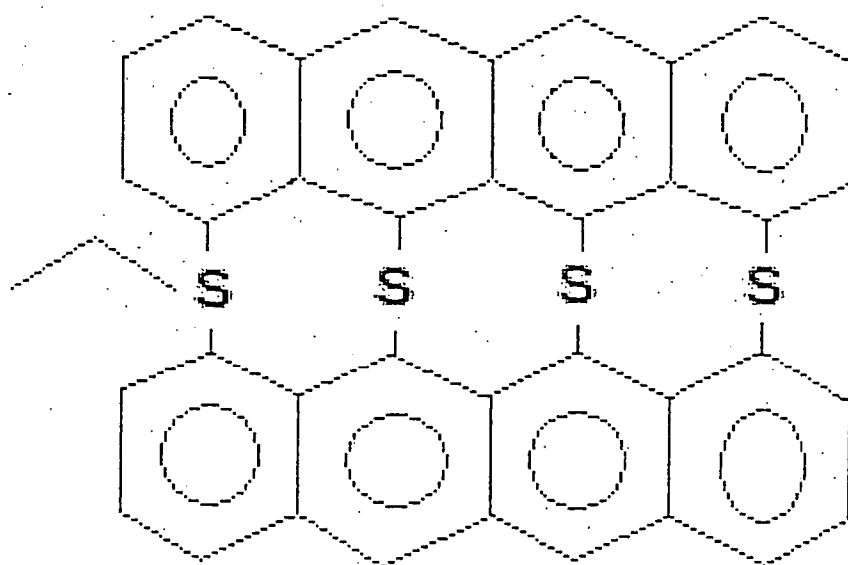


FIG. 2

A - A - A - A - B - A

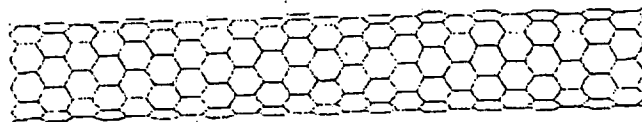


FIG. 3(a)

A - A - A - A - A - A

|

B

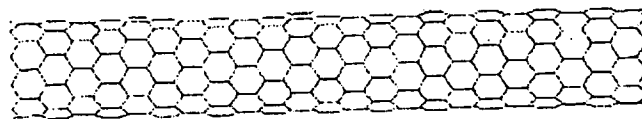
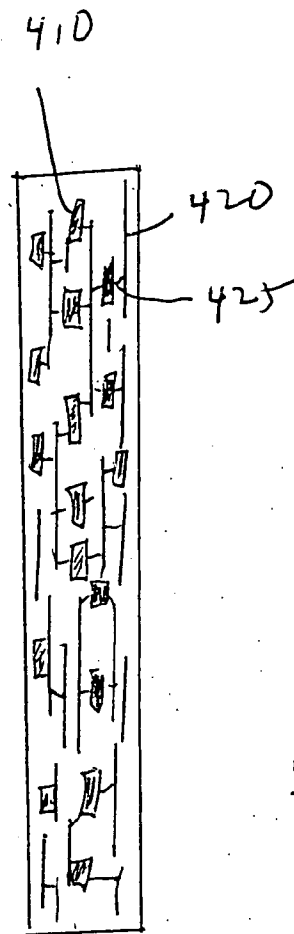


FIG. 3(b)





400

FIG. 4